standard. However, chondroitinsulfuric acid and hyaluronic acid did not exhibit a precipitation reaction with concanavalin-A.

Upon desulfation and concomitant acetylation of sodium heparinate[10] a desulfated heparin acetate is obtained which gives a precipitation reaction with concanavalin-A. This positive reaction persists when the above material is deacetylated with barium methoxide to give the N-acetyl desulfated heparin.[11] It would appear therefore that, as in the case of glycogen, the precipitation reaction reflects the over-all molecular architecture of the whole heparin molecule or part of it rather than the presence of sulfate ester groups. It is interesting to note that desulfated mucoitin acetate[10] also gives a precipitation reaction with concanavalin-A which lends support to the postulation of Jorpes[12] that heparin is a polysulfuric ester of mucoitin.

The galactogen[13] which is obtained together with heparin from beef lung does not give a precipitation reaction with concanavalin-A. It is suggested that the purity of a heparin preparation may be determined by the concanavalin-A precipitation reaction.

Experimental

Concanavalin-A Solution.—The concanavalin-A solution was prepared by extracting jack bean meal[14] with 2% saline as described previously.[3]

Concanavalin-A–Polysaccharide Precipitation Reaction.—To an aqueous solution of the polysaccharide (1 ml. containing about 1 mg. of material) is added the concanavalin solution (9 ml.). The two solutions are well mixed and then allowed to stand for 10 minutes after which time the absorbance of the turbidity produced is determined in an Evelyn colorimeter using a No. 420 filter. A blank is prepared by using water in place of the polysaccharide solution. By interpolating the absorbance produced by the precipitation reaction on a standard curve prepared in the same way using purified human liver glycogen as a standard, the ratio of the absorbancies produced by equal weights of polysaccharide and the standard glycogen is calculated.

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[11] M. L. Wolfrom, R. Montgomery, J. V. Karabinos and P. Rathgeb, THIS JOURNAL, **72**, 5796 (1950).

[12] E. Jorpes, "Heparin," Oxford University Press, London. 1939; E. Jorpes, *Biochem. J.*, **36**, 203 (1942).

[13] M. L. Wolfrom, G. Sutherland and M. Schlamowitz, THIS JOURNAL, **74**, 4883 (1952).

[14] A product of the Arlington Chemical Co., Yonkers, N. Y.

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Periodate Oxidation of Cyclic 1,3-Diketones[1]

BY M. L. WOLFROM AND J. M. BOBBITT[2]

RECEIVED NOVEMBER 2, 1955

The selective oxidizing ability of aqueous periodate ion is shown to encompass cyclic 1,3-diketones. Five- or six-membered cyclic 1,3-diketones, unsubstituted on carbon-2, reduce four molar equivalents of oxidant to yield one equivalent of carbon dioxide and one molar equivalent of a dibasic acid. Carbon-2 substituted, cyclic, six-membered 1,3-diketones reduce three molar equivalents of oxidant to yield one molar equivalent of a monobasic acid and a like amount of a dibasic acid. Postulated reaction intermediates oxidize more rapidly than the initial diketone and give the same products. Satisfactory reaction occurs between *p*H 3 and 8 with a rate maximum between *p*H 5 and 6. The kinetics were second order at low concentrations.

Oxidations of carbon compounds with aqueous periodate ion at room temperature or below can conveniently be divided into two types: (1) those producing carbon–carbon bond cleavage and (2) those where no such cleavage takes place. The second reaction type occurs when a hydrogen attached to a carbon flanked by carbonyl groups is transformed into an hydroxyl function. This gives rise to an hydroxy ketone, thus making the compound susceptible to the first type of oxidation.

The first type of periodate oxidation is the well known α-glycol cleavage reaction discovered by Malaprade[3] and initially developed by Fleury[4] and by Hudson,[5] and their associates. The same type of oxidation probably prevails in the oxidation of α-hydroxyketones,[6] α-diketones,[6] 2-aminoalcohols[7] and α-keto-acids,[8] since in each case the reduction of one equivalent of oxidant is accompanied by the cleavage of one carbon–carbon bond. The theory of this type of oxidation has been extensively studied.[9]

The second type of periodate oxidation was noted to take place in malic,[10] malonic[8,10,11] and acetoacetic acids[11] and their derivatives, and, indirectly, in malonaldehyde.[11] Other examples of this type of oxidation have appeared in the sugar series.[12] Ab-

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[1] Reported in part in *Abstracts Papers Am. Chem. Soc.*, **127**, 31N (1955).

[2] Allied Chemical and Dye Fellow, 1954–1955.

[3] L. Malaprade, *Compt. rend.*, **186**, 382 (1928); *Bull. soc. chim.*, [4] **43**, 683 (1928); [5] **1**, 833 (1934).

[4] P. Fleury and J. Lange, *Compt. rend.*, **195**, 1395 (1932); *J. pharm. chim.*, **17**, 107, 196 (1933).

[5] E. L. Jackson and C. S. Hudson, THIS JOURNAL, **58**, 378 (1936); **59**, 994 (1937); **61**, 959 (1939).

[6] P. W. Clutterbuck and F. Reuter, *J. Chem. Soc.*, 1467 (1935).

[7] B. H. Nicolet and L. A. Shinn, THIS JOURNAL, **61**, 1615 (1939); L. H. Shinn and B. H. Nicolet, *J. Biol. Chem.*, **138**, 91 (1941).

[8] D. B. Sprinson and E. Chargaff, *ibid.*, **164**, 433 (1946).

[9] R. Criegee, *Sitzber. Ges. Beförder. ges. Naturw. Marburg*, **69**, 25 (1934); *C. A.*, **29**, 6820 (1935); C. C. Price and H. Kroll, THIS JOURNAL, **60**, 2726 (1938); C. C. Price and M. Knell, *ibid.*, **64**, 552 (1942); L. J. Heidt, E. K. Gladding and C. B. Purves, *Paper Trade J.*, **121**, No. 9, 35 (1945); F. R. Duke, THIS JOURNAL, **69**, 3054 (1947); J. E. Taylor, *ibid.*, **75**, 3912 (1953); F. R. Duke and V. C. Bulgrin, *ibid.*, **76**, 3803 (1954); G. J. Buist, C. A. Bunton and V. J. Shiner, *Research*, **6**, 4S (1953); G. J. Buist and C. A. Bunton, *J. Chem. Soc.*, 1406 (1954).

[10] P. Fleury and J. Courtois, *Bull. soc. chim.*, [5] **14**, 358 (1947); [5] **15**, 190 (1948).

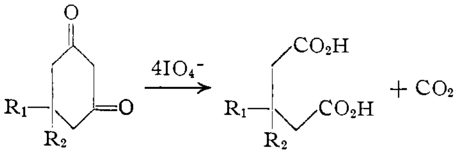
[11] C. F. Huebner, S. R. Ames and E. C. Bubl, THIS JOURNAL, **68**, 1621 (1946).

[12] C. Niemann and J. T. Hays, *ibid.*, **67**, 1302 (1945); T. G. Hallsall, E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, 1427 (1947); R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **73**, 3742 (1951); M. L. Wolfrom, A. Thompson, A. N. O'Neill and T. T. Galkowski, *ibid.*, **74**, 1062 (1952); E. L. Jackson and C. S. Hudson, *ibid.*, **75**, 3000 (1953).

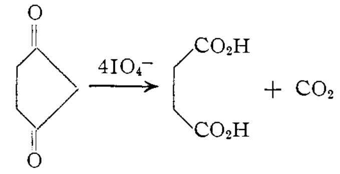
sence of reaction was noted in esters of malonic and acetoacetic acids and in the only 1,3-diketone investigated, the acyclic diketone 2,4-pentanedione.[11] In the light of this work, it was somewhat surprising when the cyclic 1,3-diketone 5,5-dimethyl-1,3-cyclohexanedione, was found to reduce periodate selectively.[13] The reaction appears to be general for cyclic five- or six-membered 1,3-diketones although an explanation for the reactivity of the cyclic over the acyclic structures can only be conjectured.

Eleven diketones have been investigated in the work reported herein. They can be divided on the basis of structure into three groups: (1) cyclic 1,3-diketones unsubstituted on C-2, (2) cyclic 1,3-diketones substituted on C-2 and (3) acyclic 1,3-diketones.

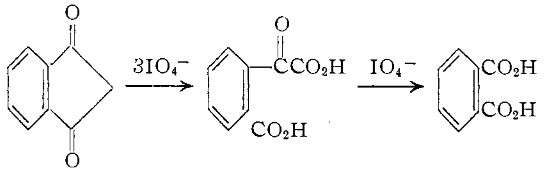
Five cyclic 1,3-diketones unsubstituted on C-2 were subjected to the action of sodium metaperiodate. These were 1,3-cyclohexanedione (I), 5-methyl-1,3-cyclohexanedione (II), 5,5-dimethyl-1,3-cyclohexanedione (III), 1,3-cyclopentanedione (IV) and 1,3-indandione (V).



I, $R_1 = R_2 = H$
II, $R_1 = CH_3$, $R_2 = H$
III, $R_1 = R_2 = CH_3$

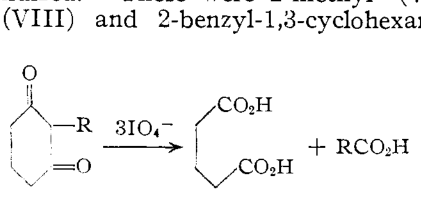


IV



V VI

Three cyclic 1,3-diketones substituted on C-2 were oxidized. These were 2-methyl- (VII), 2-ethyl- (VIII) and 2-benzyl-1,3-cyclohexanedione (IX).



VII, $R = CH_3$
VIII, $R = C_2H_5$
IX, $R = C_6H_5CH_2$

Three acyclic 1,3-diketones, 2,4-pentanedione (X), 1-phenyl-1,3-butanedione (XI) and 1,3-di-

TABLE I

ANALYTICAL DATA ON PERIODATE OXIDATIONS OF DIKETONES

	Substrate, *M*	NaIO$_4$, *M*	Temp.,[a] °C.	Time, hr.	Oxidant[b] reduced, moles per mole of substrate	Acid[c] produced. moles per mole of substrate
I	0.0178	0.1218	0	24	3.94	2.04
II	.0136	.1218		6.5	4.00	2.04
III	.0143	.1821	10	20	4.00	2.00
IV	.0048	.0609	0	96	3.92	1.92
V	.0068	.1240		48	3.64	2.08
VII	.0138	.1218		24	2.92	3.08
VIII	.0059[d]	.0609		2.75	2.95	3.05
IX	.0156[d]	.1218		24	3.04	3.04
X	.0083	.0486		24	0.60	
XI	.0073	.0486		24	.52	
XII	.0078	.0486		24	.08	
XIV	.0072[e]	.1251		7	3.03	2.02
XV	.0272	.2437		24	2.10	2.15

[a] Room temperature, 22–28°, unless otherwise stated. [b] Determined by arsenite method.[4,14] [c] By titration to phenolphthalein end-point. [d] Solution of substrate was not immediate. [e] Transient iodine appeared at higher concentrations.

TABLE II

ACID PRODUCTS FROM THE PERIODATE OXIDATION OF DIKETONES

	Substrate, *M*	NaIO$_4$, *M*	Acids[a, b] obtained	Yield, %	M.p.,[c] °C., cor.	CO$_2$,[d] moles/mole of substrate
I	0.0110	0.1268				0.98
I	.0431	.2437	Glutaric	86.5[k]	94–95[m]	
II	.0278	.2437	3-Methylglutaric[e]	90[k]	87–89[n]	1.05
III	.0301	.2483	3,3-Dimethylglutaric[f]	92[k]	101–102[o]	1.02
IV	.0100	.2437	Succinic[g]		144–145[p]	1.16
V	.0442	.2437				0.61
VI	.0455	.2500	Phthalonic[h]	18.3		
			Phthalic	18.5[l]	195–196[q]	
VII	.0176	.2481	Acetic[i]	94		0.00
			Glutaric	59[k]	95–96	
VIII	.0236	.2437	Propionic[i]	90		
			Glutaric	68[k]	95–96	
IX	.0309	.2437	Phenylacetic[j]	85[l]	75–77[r]	
			Glutaric	73[k]	95–96	
XIV	.0139	.2437	Glutaric	81[k]	94–96	1.03
XV	.0312	.2437	Glutaric	76[k]	95–96	0.99

[a] Unless otherwise noted, all final identifications were made by infrared spectral comparisons. [b] Unless otherwise noted, acids were removed from the reaction mixtures by continuous ether extraction and isolated by removal of ether and recrystallization. [c] Fisher–Johns melting point block. [d] By sweeping from the reaction mixture with a stream of nitrogen into barium hydroxide and gravimetric determination of the barium carbonate. [e] Neutral equivalent, 73.0; cyclic anhydride, m.p. 42–42.5° (accepted 41°). [f] Neutral equivalent, 80.00; cyclic anhydride, m.p. 126–127° (accepted 124°). [g] Mixed m.p. 144–145°, undepressed. [h] Isolated as aniline derivative,[15] m.p. 162.5–163.5° (accepted 165°) from concentrated ether extract after filtration of phthalic acid. [i] By steam distillation from concentrated ether extract using acetyl assay apparatus.[16] Positive identification by comparison of the infrared spectra of the sodium salts. [j] Obtained by extraction of reaction mixture with one portion of ether prior to continuous extraction. [k] After recrystallization from benzene. [l] After recrystallization from water. [m] Reported 95–96°, 97.5°. [n] Accepted 87°. [o] Accepted 103–104°. [p] Accepted 144–145°. [q] Accepted 206–208°. [r] Accepted 76.7°.

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(13) This observation was made in this Laboratory in 1952 by Dr. C. S. Rooney incidental to an investigation of the reaction products formed from reducing sugars and amino acids (Quartermaster Food and Container Institute for the Armed Forces, Chicago, Ill., Contract DA-11-009-qm-13294. The Ohio State University Research Foundation Project 477).

(14) E. L. Jackson, *Org. Reactions*, **2**, 341 (1944).

(15) R. C. Fuson, THIS JOURNAL, **48**, 1093 (1926).

(16) K. Freudenberg and M. Harder, *Ann.*, **433**, 230 (1923).

phenyl-1,3-propanedione (XII), were shown to reduce periodate ion only very slowly, if at all. This concurred with previous work.[11]

The analytical data for these oxidations are given in Table I and the product isolations are summarized in Table II.

The effect of hydrogen ion concentration on the oxidation of III was studied at room temperature in phosphate buffers. The extent of oxidation after 1, 5 and 10 hours is plotted against *p*H in Fig. 1. Satisfactory oxidation was observed between *p*H 3 and 8 with a rate maximum between *p*H 5 and 6. The periodate ion, IO_4^-, has been shown to be most prevalent in this same *p*H region.[17] These results concur with the statement[18] that "the monovalent ion is the sole reactive form of periodic acid and that the undissociated acid or the divalent ion must first be transformed to this ion before reaction can occur."

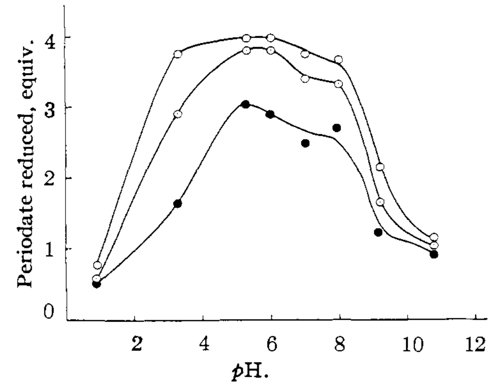

Fig. 1.—Extent of oxidation of 5,5-dimethyl-1,3-cyclohexanedione by periodate ion as a function of *p*H: ●, 1 hr.; ⊙, 5 hr.; ○, 10 hr.

The comparative oxidation rates of those cyclic diketones unsubstituted on C-2, I–IV, were measured in water at 0° and low concentration (Fig. 2).

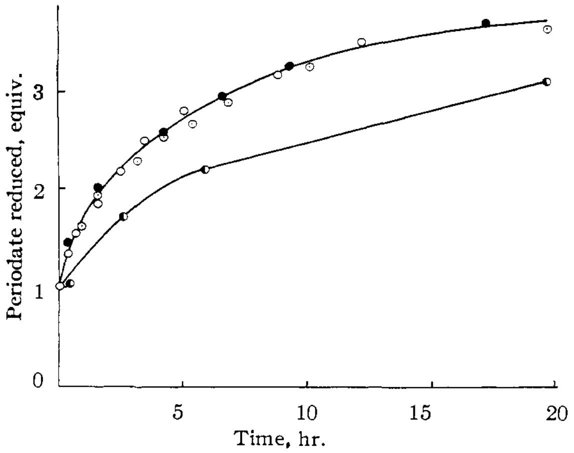

Fig. 2.—Relative rate curves from the oxidation of cyclic 1, 3-diketones unsubstituted on carbon 2: ◐, 1,3-cyclopentanedione; ○, 1,3-cyclohexanedione; ⊙, 5,5-dimethyl-1, 3-cyclohexanedione; ●, 5-methyl-1,3-cyclohexanedione.

The oxidation of IV, the cyclopentane derivative, is much slower than those of the six-membered ring compounds. As a separate group, the C-2 substituted cyclic ketones VII–IX were compared by rate measurements in buffered solution (Fig. 3). No gross differences were noted.

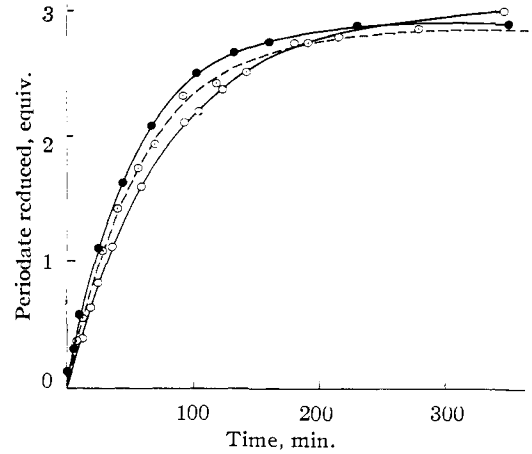

Fig. 3.—Relative rate curves for the oxidation of cyclic 1,3-diketones substituted on carbon 2: ●, 2-methyl-1,3-cyclohexanedione; ⊙, 2-ethyl-1,3-cyclohexanedione; ○, 2-benzyl-1,3-cyclohexanedione.

The oxidation of 2-methyl-1,3-cyclohexanedione (VII) was studied kinetically using the ultraviolet colorimetric method[17,19] for periodate assay. The method necessitated low concentrations. A series of reactions was carried out utilizing constant amounts of oxidant and varying excess amounts of substrate. The optical density readings at 222.5 mμ, after the subtraction of an "infinity value," are plotted in Fig. 4. From the slopes of the straight line portions of these curves, first-order rate constants were calculated. These constants were plotted against concentration of substrate (Fig, 5) to yield a straight line through the origin. Therefore, the kinetics, at these necessarily low concentrations, are first order with respect to each reactant or second order over-all.

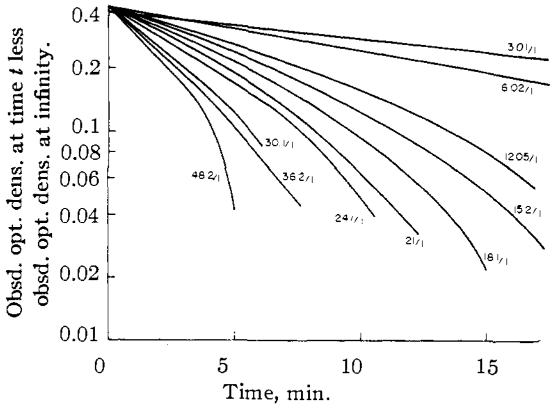

Fig. 4.—First-order reaction curves for the oxidation of 2-methyl-1,3-cyclohexanedione with sodium metaperiodate at *p*H 6.20 and 22.5°. The numbers on the curves represent the molar ratio of substrate to oxidant.

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[17] C. E. Crouthamel, A. M. Hayes and D. S. Martin, THIS JOURNAL, **73**, 82 (1951).

[18] J. E. Taylor, B. Soldano and G. A. Hall, *ibid.*, **77**, 2656 (1955).

[19] J. S. Dixon and D. Lipkin, *Anal. Chem.*, **26**, 1092 (1954).

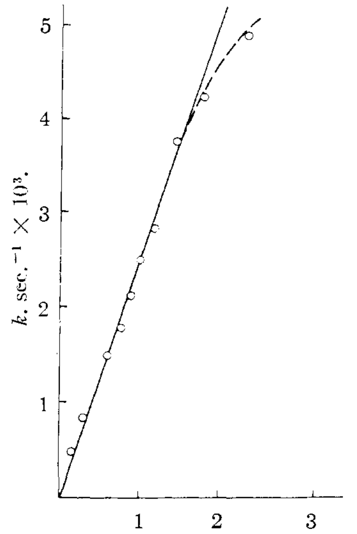
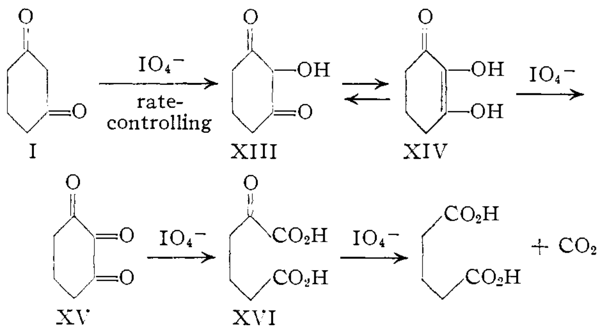


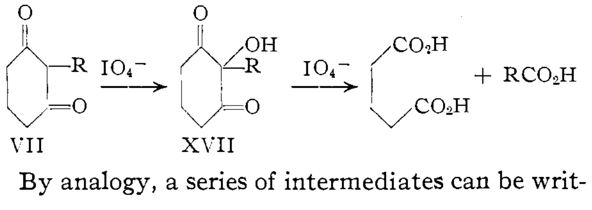
Fig. 5.—First-order rate constants (calculated from Fig. 4) *versus* concentration of 2-methyl-1,3-cyclohexanedione.

From known periodate oxidations,[3–12] the oxidation of I might well take the course.



The possible intermediates, 2,3-dihydroxy-2-cyclohexenone (XIV) and 1,2,3-cyclohexanetrione (XV), were prepared and subjected to periodate oxidation. They reduced three and two molar equivalents of periodate, respectively (Table I), and each yielded quantitative amounts of glutaric acid and carbon dioxide (Tables I and II). The relative rates of oxidation of I and its possible reaction intermediates XIV and XV were compared by measuring periodate ion colorimetrically, as before.[17,19] The optical density readings were plotted directly against time (Fig. 6). Only compound I was still removing periodate (reducing optical density) after one minute. The upward drift in the curves is probably due to a photochemical reaction.[18]

The intermediate in the oxidation of 1,3-indandione analogous to XVI, phthalonic acid (VI), was isolated from a reaction mixture after one day in 18.3% yield as its aniline derivative.[15]



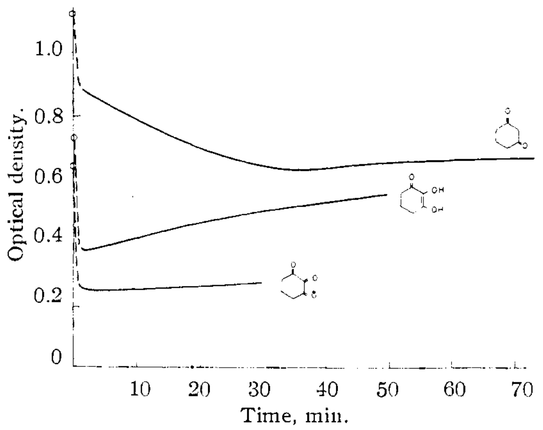
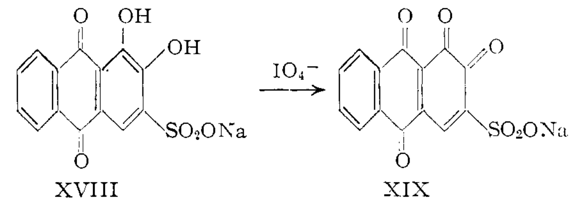


Fig. 6.—Relative oxidation rates of 1,3-cyclohexanedione and its possible reaction intermediates; O, represents theoretical starting points calculated from the sum of the optical densities of the components.

By analogy, a series of intermediates can be written for the oxidation of the C-2 substituted 1,3-cyclohexanediones.

The hydroxylation by periodate of a methylene carbon flanked by carbonyl groups, has been suggested.[10,11] The reason for its occurrence in cyclic 1,3-diketone systems and not in acyclic 1,3-diketones is uncertain. The oxidation of XIII to XV without chain scission to produce formic acid, is contrary to established periodate behavior[6] in acyclic systems, but a similar course of reaction was noted to occur as a side reaction in malonic acid oxidation.[11] The reaction can be rationalized more readily by postulating XIV as an intermediate. The structure XIV is a tautomer of XIII and is probably the prevalent structure for it.[20] The ability of the hydroxylated 1,3-diketone XIII to assume such an enediolic reductone[21] structure (XIV) probably permits further oxidation without immediate carbon–carbon bond cleavage (XIV to XV). If this reductone system cannot form, as in the carbon-2 substituted 1,3-diketones VII to IX, further oxidation is accompanied by carbon–carbon bond cleavage. Apparently, the acyclic compounds, malonic and acetoacetic acids, can only assume such a reductone structure to a small extent since their oxidation proceeds primarily like that of VII. The conclusions may then be drawn that cyclization favors the reductone structure XIV. The oxidation by periodate of such a reductone system has been observed[22] in the oxidation of 1,2-dihydroxy-3-anthraquinonesulfonate (XVIII) to 1,2,9,10-anthra-



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[20] B. Pecherer, L. M. Jampolsky and H. M. Wuest, THIS JOURNAL, **70**, 2587 (1948).

[21] H. v. Euler and C. Martius, *Svensk Kem. Tidskr.*, **45**, 73 (1933); *Ann.*, **505**, 73 (1933); H. v. Euler and H. Hasselquist, "Reduktone." Ferdinand Enke, Stuttgart, 1950.

[22] L. K. Ramachandran and P. S. Sarma, *J. Sci. Ind. Research (India)*, **10B**, 147 (1951); *C. A.*, **47**, 2160 (1953).

cenetetrone-3-sulfonate (XIX). This oxidation can be considered, in conjunction with the oxidation of XIV to XV, to be a further instance of periodate oxidation without carbon–carbon bond cleavage.

Experimental

Substrates.—5,5-Dimethyl-1,3-cyclohexanedione, m.p. 147.5–149° (accepted 148–149°), and 2,4-pentanedione were obtained commercially. The sample of 1,3-cyclohexanedione, m.p. 105–105.5° (accepted 105–106°), was provided by Professor M. S. Newman of this University and a sample of 1,3-cyclopentanedione, m.p. 149–150° after sublimation (accepted 151.5–152.5°[23]), was kindly provided by Dr. R. G. Wilkinson of the Lederle Laboratories Division of the American Cyanamid Co.

The remaining diketones were prepared: 5-methyl-1,3-cyclohexanedione,[24] m.p. 128–129° (reported[24] 128–129°); 1,3-indandione,[25] m.p. 129–130° (reported[25] 130–132°); 2-methyl-1,3-cyclohexanedione, m.p. 208–209° (reported[26] 204°); 2-ethyl-1,3-cyclohexanedione,[26] m.p. 178–179° (reported[26] 178°); 2-benzyl-1,3-cyclohexanedione,[27] m.p. 188–189° (reported[27] 184–185°); 1-phenyl-1,3-butanedione,[28] m.p. 57–58° (reported 57–58°; 61°); 1,3-diphenyl-1,3-propanedione,[28] m.p. 77–78° (reported 77–78°); 2,3-dihydroxy-2-cyclohexenone,[20] m.p. 112–114° (reported[20] 114°); and 1,2,3-cyclohexanetrione,[20] m.p. 103–104° (reported[20] 104–105°).

Effect of Hydrogen Ion Concentration (Fig. 1).—A series of phosphate buffers was prepared which gave final reaction mixture *p*H values of 0.90, 3.30, 5.30, 6.02, 7.03, 8.00, 9.40, 10.88 and 12.88.[29] Potassium salts were used above *p*H 7 and sodium salts below. The relative rates of oxidation were obtained by measuring oxidant consumption (arsenite method[4,14]) in solutions 0.0310 *M* in oxidant (sodium metaperiodate), 0.0054 *M* in substrate (5,5-dimethyl-1,3-cyclohexanedione) and 0.50 *M* in buffer. Solutions were maintained at room temperature and reactions were performed simultaneously.

Relative Oxidation Rates.—Solutions of the diketones I–IV (unsubstituted on C-2) in water were prepared and combined with sodium metaperiodate solutions at 0° to yield reaction mixtures 0.0609 *M* in oxidant and 0.0075 *M* in substrate. The relative rates of oxidation were obtained (Fig. 2) by measurement of oxidant consumption (arsenite method[4,14]).

Weighed amounts of the diketones VII–IX (substituted on C-2) were added to a reaction mixture containing one part of lithium periodate solution (obtained by neutralizing a solution of periodic acid with lithium carbonate), one part of saturated lithium acetate and two parts of acetic acid at room temperature. Compound VII was not oxidized simultaneously with VIII and IX. The reaction mixtures were 0.0620 *M* in lithium periodate and 0.00566 *M* in substrate. Periodate consumption was measured by the arsenite method[4,14] (Fig. 3).

Kinetic Studies (Fig. 4).—A series of solutions of VII in water ranging from 4.70×10^{-3} *M* to 2.04×10^{-4} *M* were prepared by successive dilution of a solution 1.88×10^{-2} *M* in VII which had been titrated to *p*H 6.2 with sodium hydroxide. A solution of oxidant, 9.75×10^{-5} *M*, was prepared and buffered to *p*H 6.20 with phosphate (0.02 *M*). Equal volumes of these solutions were mixed and relative rates were obtained by measuring the oxidant consumption colorimetrically at 222.5 mμ.[17,19,30] All solutions had been allowed to equilibrate to a constant temperature (22.5°).

Relative Rate Studies.—Aqueous solutions of the three compounds I, XIV and XV, were prepared and combined with an equal volume of sodium metaperiodate solution giving reaction mixtures 5.875×10^{-4} *M* in substrate and 4.875×10^{-5} *M* in oxidant. The optical densities at 222.5 mμ[17,19,30] of these reactions were observed at the stated time intervals (Fig. 6).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

An Anomalous Reaction of Methyl 3,4-*O*-Isopropylidene-β-D-arabinopyranoside 2-*O*-(*S*-Sodium Dithiocarbonate)

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Reaction of methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside 2-*O*-(*S*-sodium dithiocarbonate) (III) in the presence of ethyl iodide, *n*-propyl bromide, isopropyl bromide or *t*-butyl chloride did not lead to the expected 2-*O*-(*S*-alkyl dithiocarbonate) esters. The product in each case was bis-(methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside) 2-thionocarbonate (V), the structure of which is proved.

In a previous paper[2] the preparation of *O*-(*S*-alkyl dithiocarbonate) ("xanthate") esters of certain carbohydrate derivatives by the general route I → II → III → IV was described. Thus the *S*-methyl and *S*-triphenylmethyl esters of methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside 2-*O*-(dithionate) (IV, $R' = CH_3-$ and $(C_6H_5)_3CH-$, respectively) were obtained by treatment of the intermediate *S*-sodium derivative III with methyl iodide and triphenylmethyl chloride, respectively. In seeking to extend this reaction, other alkyl halides such as ethyl iodide, *n*-propyl bromide, isopropyl bromide and *t*-butyl chloride were used. The expected products were not formed but in each case bis-(methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside) 2-thionocarbonate (V, m.p. 210–211°, $[\alpha]_D$ $-254°$ in benzene) was isolated. The yield of V obtained with various alkyl halides was as follows: ethyl iodide, 58.4%, *n*-propyl bromide, 30.8%, isopropyl bromide, 69.1% and *t*-butyl chloride, 6%. This paper is concerned with the proof of structure of this unexpected product V.

Alkaline hydrolysis of V gave sirupy methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside (I) which was

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